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CHAS. J. J. FOX

ON THE COEFFICIENTS OF ABSORPTION OF THE ATMOSPHERIC GASES IN DISTILLED WATER AND SEA WATER

PART I: NITROGEN AND OXYGEN

WITH ONE PLATE

EN COMMISSION CHEZ
ANDR. FRED. HØST & FILS
COPENHAGUE

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BY

CHAS. J. J. FOX

PART I: Nitrogen and Oxygen

The present publication contains an account of the first part of an investigation into the solubility of Nitrogen and Argon, Oxygen and Carbonic Acid in sea-water; namely the absorption coefficients of Nitrogen and Argon and of Oxygen. It is known that these gases have the same molecular weight dissolved as in the Gaseous state and are dissolved without chemical reaction; for these reasons HENRY's Law holds and indeed between wide limits[1]). In the case of the Carbonic Acid, conditions are different. In the first place the partial pressure of the Carbonic Acid in the atmosphere is much smaller, in fact only $^1/_{2600}$ that of the Nitrogen and $^1/_{700}$ that of the Oxygen; and sea-water is alkaline as is well known, and therefore reacts with the Carbonic Acid. The consequence is that HENRY's Law cannot hold; except perhaps over narrow limits. It is therefore clear that the nature of the problem is quite different in the case of the Carbonic Acid and must be investigated by different methods; and it is convenient to include in the present communication the determinations of Nitrogen and Oxygen and to reserve Carbonic Acid for separate publication.

The method employed for Nitrogen and Oxygen is a modified form of ESTREICHER's[2]) adaptation of OSTWALD's[3]) method. The burette A at its upper end bears a two-way tap a, on the one hand connecting it to the tube D through which the gas for investigation is to be admitted to the burette; on the other hand the tap a connects the burette by means of the spiral C to the bulb B which contains the known quantity of water, of which the solubility coefficients for the gas, are to be determined. The spiral is of very thin glass and therefore very elastic; it allows the bulb to be agitated violently without risk of breakage.

[1]) See VAN'T HOFF, Vorlesungen über theoretische und physikalische Chemie Braunschweig 1898. Zweites Heft p. 20 ff.

[2]) ESTREICHER Zeitschrift für physikalische Chemie 31 p. 176.

[3]) OSTWALD-LUTHER, Physiko-chemische Messungen p. 274.

By means of the tap c, the spiral and the burette can be exhausted, by connecting the tube E with a TOPLER's mercury-pump. Evacuation having been accomplished in this way, the tap c is closed and the gas to be investigated is allowed to come into the Burette through the tube D, by way of the taps d and a. The tube D is capillary (1 mm. dm.); its volume between the two taps a and d is very small and found easily and accurately, merely by calculation from its length and diameter. Before E is connected to the mercury-pump this capillary is filled with water between a and d, which are then closed; this water is carried subsequently into the burette when the gas to be investigated is admitted. The object of this water is to keep the gas in the burette at all times saturated with water vapour. The manipulation of the mercury and the measurement of the pressure are provided for by means of a mercury reservoir and pressure tubing, connected to the burette by means of a glass tube F melted in at the bottom and another tube G identical with A, divided into linear millimeters and provided with an ordinary glass tap g, at the top, which opens directly to the Atmosphere.

All connections referred to in the present work were made by sealing the glass tubes together with the blowpipe; and this is always to be understood unless otherwise explicitly stated.

It is quite clear that the perfection with which the final traces of air are removed from the burette, spiral and bulb is of paramount importance in the attainment of high accuracy. In the case of the burette and spiral, evacuation is of course accomplished satisfactorily beyond question by means of the mercury-pump. But the simple method which ESTREICHER employed for freeing the bulb and water from air was found upon examination to be unreliable. Before filling the bulb with water for the investigation, ESTREICHER put in a few cc. of mercury with the object of improving the mixing, on agitation, and of so increasing the rate of absorption. The present writer found this to be unnecessary; in practice it was found that 5—10 minutes continual agitation was sufficient always to ensure equilibrium between gas and water. As a rule the bulb was shaken for 5 minutes and a reading taken, then shaken again and another reading taken; it was only very seldom that these two readings differed. If such were the case however, the shaking was continued for another 5 minutes and another reading taken.

ESTREICHER filled the bulb, the volume and weight of which were determined beforehand, with water (and the few cc. of mercury), connected it directly by means of india-rubber pressure tubing to an ordinary water-pump and boiled until about a quarter of the water had evaporated away; the tap was at this point closed and the bulb weighed again. On shaking the bulb now, the water hits the glass, in the vacuum, with the characteristic crackle. As a matter of fact

however, this simple method of ESTREICHER's does not give a perfect vacuum and a bubble of air 3—6 millimeters in diameter is left behind invariably; the crackling sound adopted by ESTREICHER in his method as the criterion of complete evacuation, is in fact, misleading. If the bulb so evacuated be opened under a mercury surface with all suitable precautions, mercury should enter the bulb and fill it; but a small residual bulb of air is always left. It is of course a well-known fact that it is not easy to obtain perfectly air-free water or in fact an air free space of any kind; it might be expected, however, that boiling and evacuating employed together, in this way, should be successful if only carried out properly and continued long enough. But an exhaustive and critical examination showed that this method always leaves a residual air-bubble of about 0.01—0.1 cc. It was noticed that under these circumstances it is very difficult to get the water to boil away tranquilly and evenly; it bumps badly even when warmed gently in a luke warm water-bath. In addition, it is very difficult to get a water pump to work quite evenly, owing to the inconstancy of the water supply; and the result is that a quantity of water always collects in the rubber tubing, where it works up and down, in effect like a sort of piston, which makes it difficult for the final traces of air to make their way out. It is suggested that ESTREICHER's values for Argon and especially Helium, may be subject to a small error due to this fact. If so it might be possible that his values for Argon are too small by something between about 0.2—5 %, for Helium by about 0.5—10 %.

WINKLER[1]) as a result of some theoretical considerations which are however, admittedly not quite conclusive, has also suspected that ESTREICHER's Helium values are possibly not quite so reliable as are those accepted for some other gases. It is therefore to be hoped that these determination will be repeated.

The two weighings, before and after filling, and the known volume of the bulb give the data for calculating the volume of water taken and the free-space above the water. This latter free-space filled with water vapour, varies with the temperature owing to the different rates of expansion of water and glass; and its volume is calculated easily for any temperature when these two temperature coefficients are known. The cubic temperature coefficient of the glass bulbs employed was actually determined by experiment to be 0.0000239 between 0° and 50°. The specific volumes of the destilled water at the different temperatures employed, were taken from LANDOLT and BÖRNSTEIN's Tables (3. Aufgabe 1905); in the case of sea-water the values were taken from KNUDSEN's Hydrographic Tables, Kopenhagen 1901 p. 39—46.

[1]) L. W. WINKLER Zeitschrift für physikalische Chemie 55 p. 344.

In the present experiments the bulb was evacuated as follows. By means of a piece of thick pressure tubing, the bulb *A* (Fig. 2) was connected to the tube *B*, and the bulb and about 1/3 of the tube then filled with the water to be investigated. The water-pump was applied to the upper end of the tube *B*. The water in both *A* and *B* were kept boiling in the vacuum say for 10—15 minutes; *A* was then of course quite full of air-free water. But it is desirable that it should be not too full; otherwise the area of water-surface to be exposed to the gas in the actual experiment, will be so small that mixing will be difficult and the rate of solution slow. In practice about 10 cc. of free-space is convenient, and in the method here described it may be adjusted at that or any other value as desired, by deflecting and partially inverting the bulb while still connected by the tubing to the tube *B*, so that a bubble of steam instead of rising to the water-surface in *B* may collect inside the bulb. When this steam-bubble of the size desired has collected, the tap is closed and the bulb disconnected from the tubing. On now opening under a mercury surface, the bulb will fill completely and not the faintest trace of air will be observable. It will also be noticed that the water hits the glass on shaking, with a report somewhat alarming in its intensity; much harder in fact than is the case when the evacuation is carried out in the simple method described by ESTREICHER. There is only one difficulty in the carrying out of the method, and that is that the boiling is rather hard on the grease used for lubricating the tap[1]). The tap must be very evenly and not too freely greased; most of it will in the process of boiling be carried up by the rising water to the surface, but enough will remain to hold the tap closed tightly, at all events if the tap be well selected.

It is necessary to make the sea-water quite neutral before introduction into the bulb otherwise the Carbonic Acid will continue to be evolved the whole time, and it will be impossible to evacuate; insoluble carbonates too, would be precipitated. To accomplish this, the alkalinity of the sea-water was determined accurately by boiling 1/2 litre with a known quantity of acid in excess, and then titrating backwards (using standard alkali solution with Phenolphthalein as indicator). The exact necessary quantity of acid — a mixture of Hydrochloric and Sulphuric Acid in the proportion of Cl to SO_4 in sea-water — was then calculated and added to the original sample of sea-water, so as to make it just neutral. The amount required, is always so small that it is without effect upon the ratio of chlorine to specific gravity.

The bulb having been filled satisfactorily with the water to be investigated, it is sealed on to the spiral; *A* and *G* having been filled

[1]) The grease employed was the now well known rubber grease (OSTWALD-LUTHER, Physiko-chemische Messungen p. 154 and TRAVER's Experimentelle Untersuchungen von Gasen. Braunschweig, 1905 p. 24).

with mercury up to the taps, and the capillary D with water between the taps a and d which are then closed, the tube E is sealed on to another tube leading to the Töpler pump as well as to the gas-holder (K Figs. 3 and 4), containing the gas for the measurements. The spiral and adjoining tubes are exhausted thoroughly; the tap c is then closed and the tap belonging to the pump also. This done, the tap k of the gas-holder is opened so that gas passes from the gas-holder up as far as the taps d and c and then afterwards by opening d and a into the burette A; the water contained in the capillary between the taps d and a is of course swept in with it. All this gas is then removed again by the pump with the object of washing out any traces of foreign gases (air e. g.) which may happen to have been occluded on the glass. Before doing this the small quantity of water is always brought back to the tap d and the latter closed, before putting into communication with the pump. Finally the burette is filled with the gas, the tap a closed and the tube E then cut with the glass knife. The apparatus which, by means of attachments to the lid, was suspended in the air during these operations (balanced by a chain running to a counterpoise, over pulleys hanging from the ceiling) is at this stage lowered into the big beaker M which serves as a water-bath. It is fitted with an Ostwald Toluol thermo-regulator and an air-blast for blowing a stream of bubbles through, to ensure good circulation (not shown in Figure). A thermometer graduated in tenths of a degree, with corrections from the Physikalische Reichsanstalt, allowed the temperature of the bath to be read off, correct to one or two hundredths, with the same telescope as was used for reading off the gas in the burette[1]):

During the measurements, the tap g must be kept open the whole time to the Atmosphere. The pressure under which the gas in the burette is measured, is of course known from the difference of level of the two mercury menisci in G and A. The two scales — in linear millimeters — must be compared with one another; simply by opening both A and G to the Atmosphere and by reading off the mercury levels in each of the tubes, with the mercury adjusted by means of the Reservoir, successively at several different points on the scale.

The burette A was calibrated beforehand, so that its volume up to any point of its linear millimeter scale could be read off from a table. For this calibration, A was cut off with the glass knife, from the rest of the instrument, a glass tap was melted on at the bottom and the whole burette filled with mercury. By now running out successive small portions of mercury and weighing each time, by reading off the gra-

[1]) The 300 millimetre scales on these tubes were very exactly and finely made by Gustav Müller, Ilmenau. Then had a volume each of about 21 cc.

duation at which the mercury niveau rests at each weighing, the necessary data for finding the volume up to any graduation were obtained and then tabulated.

The gases for the determination, Atmospheric-Nitrogen (i. e. Nitrogen containing Argon) and Oxygen, were stored up in the gas-holder K (Figs. 3 and 4) from whence they could be admitted to the burette A, as desired, through the tap k and the tube E. The Nitrogen was prepared in some experiments by passing air over red-hot copper gauze, and then over soda lime and phosphoric pentoxide as illustrated (Fig. 3). Air was drawn into L from the open atmosphere by means of the tap l, which was then turned the other way so that the air collected was put into contact with hot copper contained in the tube p; it was thence passed on through q containing soda-lime and r containing pure phosphoric oxide, to the gas-holder K quite similar to L. From K it was passed back again the same way to L, and the operation repeated over again several times. In other experiments the copper gauze was replaced by white phosphorus contained in a tube of the same shape as p which was however in this case made of Jena Geräte Glas and joined to L and q by thick india rubber pressure tubing instead of being melted on with the blowpipe. The phosphorus was warmed beforehand with a lighted match and, the reaction itself then provided sufficient heat to keep it going. This was found more convenient on the whole, than the copper gauze, which when ordinary glass tubing is used, requires rather a nice adjustment of the pressure to prevent the glass either from being blown out or in when hot. The copper gauze too, must be reduced each time or else it does not work so well. Both methods gave quite the same results for the case of distilled water and subsequently the phosphorus only was employed, as being the more convenient.

According to TRAVERS[1]) the most frequently met impurity of chemically prepared Nitrogen is a trace of Nitric Oxide; which however, is decomposed at high temperatures in contact with copper, phosphorus etc. and would therefore not be formed in the present instance.

For the preparation of the Oxygen, pure potassium permanganate was used (TRAVERS loc. cit. p. 43). It was contained in a soda-glass tube s melted on to q, in the place of the gas-holder L and the tube p, used for the Nitrogen. It was also provided with a Mercury Manometer and melted on to the TÖPLER's mercury-pump. To collect pure Oxygen for use in the experiments, the gas-holder K is first filled up to the tap k with mercury and S, q, r, then evacuated by the pump. On now warming the permanganate in S, Oxygen is gene-

[1]) M. W. TRAVERS, Experimentelle Untersuchung von Gasen, deutsch von ESTREICHER. Braunschweig 1905 p. 47.

rated, collected in K and allowed to stand for a time, so that gas occluded on the glass walls may be replaced by Oxygen. The Oxygen is then pumped out again and a fresh quantity generated; it is repeated several times, to make sure that there is only pure Oxygen present and the quantity for experiment is then collected in K for use.

The bulb having been filled with the water for the experiment (Distilled water or Sea-Water) highly evacuated, melted on to the spiral and bound firmly by copper wire, in place, on the brass rod by which it is to be agitated when in the water bath; the spiral and adjoining tubes having been evacuated by the pump, the gas is admitted to the burette together with the small quantity of water in the capillary tube D (the burette rinsed out once or twice with the gas, as described above). The taps a and d having been closed and g opened, E is cut with the glass knife and the apparatus then lowered into the water-bath in the way described above. The beaker rests on a tripod which stands on a board bearing levelling screws, so that the two graduated tubes which are very near to one another and parallel, may also always be placed in the same vertical position. This is assured easily enough by means of a series of marks, plumb line, spirit level etc. suitably arranged.

By means of a telescope in front and a light placed behind the beaker, the temperature indicated by the thermometer is read off, then the mercury levels in the two tubes and finally the temperature again. This series of readings is then repeated two or three times at intervals of a few minutes. This having been done the tap a is then turned so that the gas flows into the spiral c up as far as the tap b.

The Volume of the spiral is given by the expression

$$\text{Vol. of spiral at } t_2^0 = \frac{p_1}{p_2} \cdot \frac{273 + t_2}{273 + t_1} \cdot V_1 - V_2$$

Where $V_1 V_2$ are the volumes indicated by the burette readings before and after opening the tap a, $p_1 p_2 t_1 t_2$ the corresponding corrected pressures and temperatures.

A new series of readings is then taken in the same way as before and finally the tap b of the bulb opened to the gas. The bulb is agitated vigorously with the hand by means of the lever t for 5 minutes, and a reading then taken; it is then shaken again for 5 minutes and another reading taken, which as a rule did not differ from the first reading. If it did however, shaking for another 5 minutes always gave the same reading as the second. Then the temperature of the bath was altered by about 5 degrees (the thermo-regulator adjusted suitably) and the readings continued in the same way. In some experiments the order of taking the temperatures was air temperature (14°—25° about) 25°, 35°, 45°, 50°, 40°, 30°, 20°, 10°.

5°, 0°. The idea of this was that if phenomena connected with over- or under-saturation were of any importance, it would be discovered at once by a resulting regular uneveness of the solubility curves. No such effect was ever noticeable and when this fact had been ascertained the temperature order was altered so that the low temperatures were all taken before the high ones; and because it was noticed that the grease of the taps softened considerably at higher temperatures, so that there appeared a slight risk of losing a series of determinations from that cause. This never happened fortunately. The barometer was read about every hour as a rule; more frequently if necessary. After the series of observations had been taken, the bulb was cut off from the apparatus and in the case of sea-water samples, the Chlorine of the water determined by titration (MOHR's method and KNUDSEN's tables with Normal-Water).

The apparatus has slight advantages over that employed by ESTREICHER. It is with the present apparatus not necessary always to read off the gas volume at atmospheric pressure, as ESTREICHER had to do. In practice it is very difficult to get water and gas just in equilibrium just at atmospheric pressure. By having the two graduated tubes as used here, it is possible to take any pressure and to vary it as desired (within a range of 300 millimeters). It is then, possible to set the mercury levels just about where they are desired, then to agitate the bulb until equilibrium is reached and to read off at whatever final position the mercury has taken up. This is much easier in practice and must be more accurate. It is especially of importance in the case of Oxygen which, as is well known, it is peculiarly difficult to measure with high precision in contact with a mercury surface. The reasons for this, which are somewhat obscure, are no doubt connected with Oxygen's remarkable activity chemically. In the present case it is possible by having two graduated tubes, to make sure that such possible errors are excluded, merely by making each determination at two or three different pressures. In the present case too, the quantity of water taken is greater than in the case of ESTREICHER's Experiments (130 cc. instead of about 80 cc.). To keep the gas in the burette always saturated with water vapour, ESTREICHER by suitable manipulation got a few drops over from the bulb through the spiral. In the apparatus here employed a known quantity was added beforehand by filling the tube *D*. This was found much more convenient in practice.

Finally, it should be stated that the apparatus was used and tested for several weeks and many series of determinations taken and rejected, before it was considered that everything was in perfect order and satisfactory. Then the actual determinations, particulars of which it is the purpose of the present paper to describe, were made.

The measurements of Nitrogen and Oxygen in distilled water are given in detail to illustrate the method.

Only the final results of the determinations in sea-water are given and at the same time the values as found from the formula calculated from the observations. Tables 1 and 2 contain the determinations for Nitrogen and distilled water, Table 3 for Nitrogen and sea-water of Chlorine concentration 7.25, 15.32, 23.41 ‰. Tables 4 and 5 contain the determinations of Oxygen in distilled water and Table 6 of Oxygen in sea-water of Chlorine concentration 7.68, 14.27, 20.31 ‰. In calculating these values from the observations the average composition of Air, freed from water vapour and carbonic acid, was assumed to be 79.10 % Nitrogen and 20.90 % Oxygen, by Volume.

The interpolation formulae calculated from these observations between 0° and 30° are for Nitrogen

$$N_2 = 18.561 - 0.4280\,t + 0.0074527\,t^2 - 0.00005494\,t^3 - Cl\,(0.2149 - 0.007117\,t + 0.0000952\,t^2)$$

for Oxygen

$$O_2 = 10.291 - 0.2809\,t + 0.006009\,t^2 - 0.0000632\,t^2 - Cl\,(0.1161 - 0.003922\,t + 0.000063\,t^3).$$

Table 1

Atmospheric Nitrogen in distilled water

Volume of bulb empty at 0° = 138.686 = v_0.
Volume of water taken at 0° = 123.498 = w_0.
Volume of gas taken, N_2 (corrected) = 17.630 cc. at 9°.80 and 857.95 mm.
= 19.2124 at 0°.760.
Volume remaining in Burette after opening first tap (corrected) = 14.8495 at 9°.90 and 788,3 mm.
∴ Volume of Spiral = 4.244 at 9°.90 = 4.243 at 0° = 4.248 at 50°.

t	w_t	v_t	Burette reading	Volume unabsorbed (cc. at t^0)	p = Pressure (corrected)	Volume unabsorbed (cc. at t^0 760 mm.)	Volume of gas taken (cc. at t^0, 760)	Volume absorbed at p (t^0 760)	α = absorption coeff. Volume absorbed by 1000 cc. at 760 (cc. at 0°.760)	0.7910 α	calculated
0.53	123.510	138.689	2.410	21.832	59.220	17.012	19,250	2.238	23.21	18.36	18.34
6.00	123.502	138.705	2.788	22.235	60.100	17.583	19.635	2.052	20 56	16.26	16.25
10.00	123.531	138.719	3.330	22.762	60.107	18.002	19.916	1.914	18.90	14.94	14.97
15.72	123.619	138.739	3.454	22.818	61.550	18.480	20.319	1.839	17.37	13.74[1]	13.46
20.60	123.732	138 754	4.184	23.440	61.489	18.965	20.662	1.697	15.76	12.46	12.43
24.90	123.857	138.769	4.254	23.401	62.750	19.321	20.965	1.643	14.73	11.65	11.68
29.88	124.030	138.786	4.559	23.561	63.020	19.537	21.315	1.578	13.83	10.94	10.96
34.99	124.236	138.802	5.304	24.117	63.460	20.138	21.675	1.537	13.12	10.38	10.36
41.49	124.536	138.823	6.113	24.647	63.680	20.652	22.132	1.480	12.31	9.74	9.71
46.79	124.807	138.841	6.817	25.099	63 822	21.077	22.505	1.428	11.63	9.20	9.22
49 89	124.928	138.851	7.277	25.438	63.700	21.321	22.723	1.402	11.33	8.96	8.94

[1]) This observation was rejected; it is obviously affected by some exceptional error.

Table 2

Atmospheric Nitrogen in distilled water

Volume of bulb empty at 0° = 138.686 = v_0.
Volume of water taken at 0° = 125.1995 = w_0.
Volume of gas taken, N_2 (corrected) = 18.250 cc. at 13°.94 and 856.1 mm. = 19.559 at 0°.760.
Volume remaining in Burette after opening first tap (corrected) = 15.501 at 14°.02 and 784.5 mm.
∴ Volume of Spiral = 4.420 at 14° = 4.419 at at 0° = 4.4255 at 50°.

t	w_t	v_t	v_{Hg}[1])	Burette reading	Volume unabsorbed (cc. at t^0)	p = Pressure (corrected)	Volume unabsorbed (cc. at t^0 760 mm.)	Volume of gas taken (cc. at t^0 760)	Volume absorbed at p (t^0 760)	α = absorption coeff. Volume absorbed by 1000 cc. at 760 (cc. at 0°,760)	0.7910 α	calculated
0.39	125.213	138.687	1.556	3.194	19.531	66.294	17.037	19.587	2.550	23.31	18.44	18.40
4.40	125.200	138.704	1.557	3.490	19.860	66.929	17.490	19.874	2.384	21.28	16.83	16.82
7.40	125.211	138.711	1.558	3.708	20.070	67.457	17.815	20.089	2.274	19.92	15.76	15.79
10.90	125.244	138.722	1.558	4.002	20.340	67.906	18.177	20.340	2.163	18.58	14.70	14.71
12.80	125.271	138.730	1.559	3.177	19 498	71.206	18.269	20.476	2.207	17.96	14.21	14.19
14.25	125.295	138.733	1.559	4.195	20.495	68.614	18.503	20.580	2.077	17.45	13.80	13.82
19.60	125.411	138.748	1.561	5.924	22.123	65.738	19.135	20.963	1.828	15.73	12.44	12.42
23.30	125.517	138.764	1.561	4.396	20.504	71.512	19.293	21.228	1.935	15.09	11.94	11.94
29.90	125.740	138.786	1.563	6.830	22.737	66.773	19.976	21.701	1.725	10.84	10.82	10.82
35.76	125.981	138.805	1.564	5.635	21.319	72.581	20.306	22.121	1.761	12.95	10.24	10.28
40.28	126.317	138.819	1.565	8.177	23.538	67.312	20.847	22.445	1.597	12.44	9.84	9.82
45.73	126.470	138.839	1.566	6.832	22.059	72.779	20.167	22.835	1.668	11.79	9.33	9.32
48.70	126.640	138.847	1.566	9.157	24.252	67.189	21.439	23.048	1 509	11.44	9.05	9.05
52.01	126.827	138.858	1.567	9.887	24.776	66.919	21.816	23.285	1.469	11.05	8.74	8.73

[1]) In this experiment a small quantity of mercury was placed in the bulb before the water sample, with the object of helping mixing, in accordance with Estreicher's practice.

Table 3

Nitrogen and Sea-water

Cl = 7.25			Cl = 15.32			Cl = 23.41		
t	observed	calculated	t	observed	calculated	t	observed	calculated
0.33	16.88	16.86	0 61	15.24	15 29	0.31	13.51	13.50
5.81	15.00	15.03	6.38	13.50	13 46	7.41	11.82	11.86
13.10	13.16	13.11	11.91	12.23	12.22	11.52	11.15	11.13
18.49	12.04	12.01	17.61	11.23	11.21	14.68	10.70	10.65
24.11	11.02	11.09	22.69	10 44	10.48	22.20	9.72	9.71
27.14	10.69	10.67	26.55	10.08	10 00	28.00	9.11	9.10
30.59	10.25	10.25	29.68	9.60	9.66	33.08	8.60	8.61

On comparing these results with those obtained by other workers in the case of distilled water, several points and interesting differences call for notice. In the case of Nitrogen the most modern determina-

Table 4

Oxygen in distilled water

Volume of bulb empty at 0° = 138.686 = v_0.
Volume of water taken at 0° = 127.9645 = w_0.
Volume of gas taken, O_2 (corrected) = 19.370 cc. at 5°.40 and 952.6 mm.
= 23.8078 at 0° and 760 mm.
Volume remaining in Burette after opening first tap (corrected) = 16.295 at 15°.43 and 903.7 mm.
∴ Volume of Spiral = 4.8580 at 15°.43 = 4.8565 at 0° = 4.8615 at 50°.

t	w_t	v_t	Burette reading	Volume absorbed (cc. at t°)	p = Pressure (corrected)	Volume absorbed (cc. at 0° 760 mm.)	Volume of gas taken (cc. at t° 760)	Volume absorbed at p (= 760)	α = absorption coeff. Volume absorbed by 1000 cc. at 760 (cc. at 0° 760)	0.2000 α	calculated
0.61	127.976	138.689	2.973	18 541	73.57	17.824	23.861	6 037	48.61	10.16	10.13
0.81	127.975	138.690	6.142	22.713	62.80	18.768	23 878	5.110	48.18	10.07	10.08
5.51	127.967	138.705	3.953	19.559	73.51	18.911	24.288	5.377	42 58	8.90	8 92
5.60	127.967	138.707	11.285	26.882	56.95	20.144	24.296	4.152	42.58	8.90	8.90
10.82	128.009	138.722	8.018	23.578	65 77	20.404	24.751	4.347	37.75	7.87	7.88
10.90	128.014	138.723	3.983	19 559	76.54	19.698	24.758	5.060	37.76	7.89	7.86
15.60	128.088	138.739	7.467	23.075	69.12	20.986	25.168	4.182	33.97	7.10	7.14
15.60	128.088	138 739	4.578	20.086	77.54	20.443	25.168	4.725	34.21	7.15	7.14
20.80	128.213	138.755	5.242	20.643	78 12	21.219	25.622	4.403	31.05	6.49	6.48
20.81	128.213	138.755	9.160	24.611	67.44	21.839	25 623	3.784	30 91	6.46	6.48
26.00	128.375	138 773	5.933	21 204	78.62	21.935	26.075	4.140	28.47	5.95	5.94
26.00	128.375	138.773	10.416	25.673	66.76	22 553	26.075	3.522	28.52	5.96	5.94
30.98	128.560	138.789	10.425	25.513	69.16	23.227	26.509	3.282	25.19	5.26	5.26
31.04	128.562	138 790	6 359	21.446	80.43	22.696	26 515	3.819	25.17	5.26	5.26
35.49	128.752	138.804	6.851	21.763	80.66	23.098	26.903	3.805	24.65	5.15	5.16
35.59	128.756	138.805	11.231	26.140	68.80	23.664	26 911	3.247	24.66	5.15	5.15
40.04	128.966	138.818	11.228	25.930	70.62	24.095	27.299	3.204	23.32	4.87	4.87
40.09	128 970	138.819	7.127	21.936	81.76	23.598	27.304	3.706	23.30	4.87	4.86
45.29	129.242	138.836	11.416	25.871	72.30	24.611	27.757	3.146	21.95	4.59	4.58
45.29	129.242	138.836	7.697	22.151	82.89	24.159	27.757	3.598	21.90	4.58	4.58
50.25	129.523	138.852	7.116	22.307	83.99	24.652	28.190	3.538	20.88	4.36	4.37
50.29	129.527	138 854	11.806	26.094	73.14	25.112	28.193	3.081	20 88	4.36	4.37

tions are those of WINKLER[1]) and of BOHR and BOCK[2]) both of them evidently carried out with the utmost refinement and precision. There are several older determinations, good in their day but made by less perfect methods; omitting those of BUNSEN which now only have historic value, those of DITTMAR[3]), TORNÖE[4]), HAMBERG[5]) and of PETTERSSON and SØNDEN[6]) may be mentioned. On comparing all these

[1]) Berichte d. Deutschen Chemischen Gesellschaft 22. (1889). 1766.
[2]) WIEDEMANN's Annalen 44. (1891). 316.
[3]) CHALLENGER Expedition. Physics and Chemistry. Vol. 1, p. 172.
[4]) Den norske Nordhavs Expedition. 1876—1878. Chemistry.
[5]) Bihang til K. Svenska Vet. Akad. Handlinger 10. No. 13. 1885.
[6]) Svensk kemisk Tidskrift. 1889, p. 17.

Table 5

Oxygen in distilled water

Volume of bulb empty at 0° = 138.2724 = v_0.
Volume of water taken at 0° = 127.4260 = w_0.
Volume of gas taken, O_2 (corrected) = 19.965 cc. at 16°.40 and 978.15 mm.
= 25.1071 at 0° and 760 mm.
Volume remaining in Burette after opening first tap (corrected) = 16.615 at 16.54 and 900.6 mm.
∴ Volume of Spiral = 6.060 at 16°.54 = 5.058 at 0° = 5.062 at 45°.

t	w_t	v_t	Burette reading	Volume unabsorbed (cc. at $t°$)	p = Pressure (corrected)	Volume unabsorbed (cc. at $t°$ 760 mm.)	Volume of gas taken (cc. at $t°$ 760)	Volume absorbed at p ($t°$ 760)	α = absorption coeff. Volume absorbed by 1000 cc. at 760 (cc. at 0° 760)	0.2090 α	calculated
1.63	127.432	138.278	3.930	19.834	74.34	19.329	25.257	5.928	47.27	9.88	9.85
2.18	127.429	138.281	8.162	24 071	64.06	20.289	25.308	5.019	46.36	9.69	9.71
6.20	127.430	138.293	4.468	20.390	75.50	20.256	25.677	5.421	41.87	8 75	8.76
6.60	127.433	138.297	8.771	24.694	64.88	21.081	25.714	4.633	41.58	8.69	8.68
9.53	127.456	138.304	4.766	20.673	76.58	20.831	25.983	5.152	38.76	8.10	8.11
9.61	127.457	138.306	9.084	24.992	65.61	21.576	25.991	4.415	38.76	8.10	8.10
13.65	127.513	138.318	8.086	24.951	67.45	22.144	26 362	4.218	35.50	7.42	7.42
13.75	127.515	138.319	6.040	21.904	78.09	22.506	26.372	4.866	35.36	7.39	7.41
16.72	127.573	138.328	5.750	21.565	77 61	22.022	26.645	4.623	33.44	6.99	6.98
16.75	127.573	138.329	10.111	25.927	66.54	22.700	26.647	3.947	33.30	6.96	6 98
23.80	127.762	138.351	6.125	21 775	80.11	22.953	27.296	4.343	29.67	6.20	6.16
23.90	127.765	138.353	10.569	26.217	68.43	23.606	27.305	3.699	29.57	6.18	6.15
29.86	127.974	138.372	11.184	26.643	69.62	24.406	27.853	3.447	26.51	5.54	5.58
29.88	127.975	138.373	7.204	22.763	79.74	23.883	27.855	3.962	26.60	5.56	5.58
37.51	128.303	138.397	11.572	26.738	71.74	25.239	28.587	3.318	24.09	5.03	5.03
37.54	128.304	138 398	7.553	22.719	82.23	24.761	28.559	3.798	24.06	5.03	5.03
43.25	128.587	138.466	8.188	23.129	83.52	25.418	29.085	3.667	22.41	4.68	4.69
43.29	128.591	138.467	12.395	27.534	71.59	25.936	29.088	3.152	22.40	4.68	4.68

Table 6

Oxygen and Sea-water

Cl = 7.68			Cl = 14.27			Cl = 20.31		
t	observed	calculated	t	observed	calculated	t	observed	calculated
0.32	9.36	9.32	0 44	8.50	8.54	0.47	7.89	7.84
4.96	8.09	8.07	5.32	7.53	7.57	6.10	6.81	6.86
12.22	7.00	7.04	11.98	6.60	6.56	12.03	6.02	6.08
16.36	6.46	6.50	14.36	6.28	6.28	14.89	5.84	5.78
21.22	5.93	5.96	20.10	5 70	5.66	19.86	5.33	5.30
26.84	5.56	5.52	25.31	5.22	5.19	26.02	4.75	4.78
30.22	5.13	5.13	30.66	4.76	4.72	31.02	4 35	4.36

investigators results and it is noticed firstly that WINKLER's and BOHR and BOCK's values are appreciably lower than the older values obtained

by former workers. Then again WINKLER's values are appreciably lower than BOHR and BOCK's. The present writer's values lie between those of WINKLER and of BOHR and BOCK. On comparing the methods employed by the different workers it must be noted that all of the older methods mentioned, were carried out by bubbling air through the water and then extracting the air and measuring the volume. This method has the advantage that it is strictly analogous to the action between sea-water and the Atmosphere in Nature; the chief disadvantage is that it is not easy to tell when exact equilibrium is reached. In any case the gas-phase as well as the liquid-phase really ought to be analysed whenever this kind of method is employed. BOHR and BOCK also used the same method but with greater refinement and precision. On the other hand the values of WINKLER and the present writer were obtained by shaking the gas with the liquid and then measuring the contraction; in effect an analysis of the gaseous-phase, while the other method may be regarded as an analysis of the liquid-phase. If only pure gases are concerned, both methods may be expected to give the same result under good conditions; and in this connection it may be noticed that all methods tend in the case of Oxygen to give more concordant values than in the case of Nitrogen. And the reason for the difference in the latter case is to be sought in the fact that Atmospheric-Nitrogen is not a pure substance but contains 1.185 % of Argon[1]), the solubility of which is more than double that of Nitrogen at 0° and which falls off with the temperature at a different rate. Unfortunately it is not possible to tell from the accounts accessible to the present writer, whether WINKLER's Nitrogen was chemically prepared or obtained from the Atmosphere.

In the case of determinations made by the method adopted also by BOHR and BOCK, it is clear that both the Nitrogen and Argon always have at all temperatures the partial pressure they have in the open air. On the other hand in the absorption methods employed by WINKLER and the present writer, the amounts of Nitrogen and Argon actually dissolved in the liquid-phase at different temperatures is different and varies differently with the temperature. The result is that by these methods the percentage of each left over in the gaseous-phase will also be different at different temperatures, by a corresponding amount; and the partial pressures to that extent different for different temperatures, instead of constant and the same as that of the air, as in BOHR and BOCK's method. The writer only noticed this point after having calculated the formula from his observations and upon then comparing the results with those found by the other investigators[2]).

[1]) TRAVERS loc. cit. p. 116.

[2]) Dr. ERNST RUPPIN, Kiel has noticed this point too and was also kind enough to call the writer's attention to it by letter.

The differences may be represented by the following formula for Atmospheric-Nitrogen of partial pressure 0.7910 of an atmosphere.

$$x = \frac{0.7910 \times 1.185}{100} (\alpha_1 - \alpha_2) = 0.009373 (\alpha_1 - \alpha_2)$$

Where x represents the no. of cc. to be added to the value obtained by the method employed by the writer, to make it comparable with that employed by Bohr and Bock, in which the Nitrogen always at all temperatures has a constant partial pressure of 0.7816 and Argon a constant partial pressure of 0.0094 of an atmosphere. α_1 and α_2 are the absorption coefficients concerned, of Argon and of Atmospheric-Nitrogen respectively. Those for Argon have been determined by Estreicher by the same method as used by the present writer. This correction was calculated for every degree; it was found to be 0.322 ‰ at 0°, 0.239 at 10°, 0.197 at 20° and 0.169 at 30°. This correction is also included in Tables 8 and 11.

In Table 7 are to be found values for Atmospheric-Nitrogen, according to determinations of Winkler and the writer, corrected and uncorrected by this amount, required to make the values correspond to a constant partial pressure of pure Nitrogen equal to 0.7816 of an atmosphere plus a constant partial pressure of Argon equal to 0.0094 of an atmosphere; the two together making up a constant Atmospheric-Nitrogen partial pressure equal to 0.7910 of an atmosphere. As stated already, there is in view of the fact that it is unknown how the Nitrogen was prepared, no difinitely satisfactory reason for applying this particular correction to Winkler's determinations; the Nitrogen used by him may very well have been prepared chemically and therefore quite free from Argon. In that case the true correction necessary would of course be even larger, but only by 0.04 cc. ‰; and this is of no importance. There is therefore sufficient reason for including in the Table, Winkler's determinations with the given correction added.

Table 7

Solubilities in distilled water of Atmospheric Nitrogen
(Nitrogen, 0.7816 atmosphere + Argon, 0.0094 atmosphere)

t	Winkler		Bohr & Bock	Fox		Hamberg	Dittmar
	uncorrected	corrected		uncorrected	corrected		
0	18.57	18.89	18.89	18.56	18.88	19.14	19.30
5	16.46	16.73	17.03	16.60	16 87	16.93	17.10
10	14.69	14.93	15.47	14.97	15.21	15.14	15.37
15	13.30	13.51	14.13	13.63	13.84	13.73	13.96
20	12.20	12.40	12.97	12.54	12.74	12.63	12.81
25	11.32	11 50	11.90	11 66	11.84	11 81	11.83
30	10.60	10.77	10.92	10.94	11.11	—	10.99

It then appears that the values of the writer lie between those of Bohr and Bock and Hamberg and that all of them are very near to one another. Winkler's and Dittmar's also are not much different; the former's agree especially well at the lower temperatures the latter's at the higher temperatures. An inspection of all of them together, makes it seem probable that the absorption coefficients in distilled water may be regarded now as very well known, probably correct to 0.1 cc ‰ Absolute.

In the case of sea-water the coefficients hitherto in use are those of Hamberg, whose table has been doing excellent service in Oceanography since its publication in 1885[1]).

Dittmar and Tornöe had also both made determinations before, but without determining the Chlorine of their samples; they are for this reason of no value.

Table 8 contains a comparison of the values found by Hamberg and the present writer for waters of Chlorine equal to 5.52, 11.06, 16.60 and 19.38 ‰ (Hamberg's Salinities of 10, 20, 30, 35 ‰). It will

Table 8

t	Cl = 5.52		11.06		16.60		19.38	
	Hamberg	Fox	Hamberg	Fox	Hamberg	Fox	Hamberg	Fox
0	17.71	17.71	16.45	16.52	15.34	15.31	14.85	14.65
5	15.76	15.69	14.70	14.87	13.75	13.84	13.32	13.31
10	14.16	14.21	13.26	13.53	12.44	12.67	12.06	12.20
15	12.88	13.00	12.10	12.42	11.38	11.68	11.04	11.29
20	11.87	12.02	11.17	11.53	10.54	10.90	10.25	10.56
25	11.09	11.21	10.45	10.78	9.88	10.23	9.62	9.93

be seen that the agreement is on the whole very good, especially for low temperatures and low salinities. Hamberg's salinities are no doubt rather uncertain, when compared with modern work.

Table 9

	Winkler	Dittmar	Bohr & Bock	Jakobsen	Fox
0	10.25	10.25	10.32	10.06	10.29
5	8.98	8.99	9.14	8.80	9.03
10	7.97	8.00	8.11	7.79	8.02
15	7.16	7.20	7.28	7.01	7.22
20	6.50	6.53	6.59	6.39	6.57
25	5.96	5.97	6.04	5.89	6.04

[1]) loc. cit.

Table

No. of cc. of Nitrogen (including Argon) absorbed by 1000 g

°	Cl = 0	Cl = 1	Cl = 2	Cl = 3	Cl = 4	Cl = 5	Cl = 6	Cl = 7	Cl = 8	Cl = 9
−2	19.79	19.56	19.33	19.10	18.87	18.64	18.41	18.18	17.95	17.7
−1	19.33	19.10	18.88	18.66	18.44	18.22	17.99	17.77	17.55	17.3
0	18.88	18.67	18.45	18.24	18.02	17.81	17.59	17.38	17.16	16.9
1	18.45	18.24	18.03	17.83	17.62	17.41	17.20	16.99	16.78	16.5
2	18.03	17.83	17.63	17.43	17.23	17.03	16.83	16.63	16.42	16.2
3	17.63	17.44	17.24	17.05	16.85	16.66	16.47	16.27	16.08	15.8
4	17.24	17.06	16.87	16.68	16.49	16.31	16.12	15.93	15.74	15.5
5	16.87	16.69	16.51	16.32	16.14	15.96	15.78	15.59	15.42	15.2
6	16.51	16.33	16.16	15.98	15.81	15.63	15.45	15.28	15.10	14.9
7	16.17	16.00	15.83	15.66	15.49	15.32	15.15	14.98	14.81	14.6
8	15.84	15.67	15.51	15.34	15.18	15.02	14.85	14.69	14.52	14.3
9	15.52	15.35	15.20	15.04	14.88	14.72	14.56	14.40	14.24	14.0
10	15.21	15.05	14.91	14.75	14.60	14.44	14.29	14.13	13.98	13.8
11	14.92	14.76	14.62	14.47	14.32	14.17	14.02	13.87	13.72	13.5
12	14.64	14.49	14.35	14.20	14.06	13.91	13.77	13.63	13.48	13.3
13	14.36	14.22	14.08	13.94	13.80	13.66	13.52	13.39	13.25	13.1
14	14.10	13.96	13.83	13.70	13.56	13.42	13.29	13.16	13.03	12.8
15	13.84	13.71	13.58	13.45	13.32	13.19	13.06	12.94	12.81	12.6
16	13.61	13.48	13.35	13.23	13.10	12.98	12.85	12.73	12.60	12.4
17	13.38	13.25	13.13	13.01	12.89	12.77	12.64	12.52	12.40	12.2
18	13.15	13.03	12.92	12.80	12.68	12.56	12.44	12.33	12.21	12.0
19	12.94	12.83	12.71	12.60	12.49	12.37	12.26	12.14	12.03	11.9
20	12.74	12.63	12.52	12.41	12.30	12.18	12.08	11.96	11.85	11.7
21	12.54	12.43	12.33	12.22	12.11	12.00	11.90	11.79	11.68	11.5
22	12.36	12.25	12.15	12.04	11.94	11.83	11.73	11.62	11.52	11.4
23	12.18	12.07	11.97	11.87	11.77	11.67	11.57	11.47	11.36	11.2
24	12.00	11.90	11.80	11.70	11.60	11.51	11.41	11.31	11.21	11.1
25	11.84	11.74	11.65	11.55	11.44	11.36	11.26	11.16	11.07	10.9
26	11.68	11.59	11.50	11.40	11.30	11.21	11.12	11.02	10.93	10.8
27	11.53	11.44	11.35	11.26	11.16	11.07	10.98	10.88	10.79	10.7
28	11.38	11.29	11.20	11.11	11.02	10.93	10.84	10.75	10.66	10.5
29	11.24	11.15	11.07	10.98	10.89	10.80	10.72	10.63	10.54	10.4
30	11.11	11.03	10.94	10.85	10.76	10.68	10.60	10.51	10.42	10.3

In the case of the Oxygen the presence or absence of Argon has never had any influence upon older determination. For this reason perhaps, the values of different investigators have shown better agreement with one another than was the case with Nitrogen. Table 9 contains values for Oxygen, of partial pressure 0.2090 of an atmosphere, in distilled water, obtained in the most modern investigations.

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of sea-water from a free dry Atmosphere of 760 mm. pressure

Cl = 10	Cl = 11	Cl = 12	Cl = 13	Cl = 14	Cl = 15	Cl = 16	Cl = 17	Cl = 18	Cl = 19	Cl = 20
17.49	17.26	17.03	16.80	16.57	16.34	16.11	15.89	15.66	15.43	15.20
17.11	16.88	16.66	16.44	16.22	16.00	15.77	15.55	15.33	15.11	14.88
16.73	16.52	16.30	16.09	15.87	15.66	15.44	15.23	15.01	14.80	14.58
16.37	16.16	15.95	15.75	15.54	15.33	15.12	14.92	14.71	14.50	14.29
16.02	15.82	15.62	15.42	15.22	15.02	14.82	14.61	14.41	14.21	14.01
15.69	15.49	15.30	15.11	14.91	14.72	14.52	14.33	14.13	13.94	13.74
15.37	15.18	14.99	14.80	14.61	14.43	14.24	14.05	13.86	13.67	13.49
15.05	14.87	14.69	14.51	14.33	14.14	13.96	13.78	13.60	13.42	13.24
14.76	14.58	14.40	14.23	14.05	13.87	13.70	13.52	13.35	13.17	13.00
14.47	14.30	14.13	13.96	13.79	13.62	13.45	13.28	13.11	12.94	12.77
14.19	14.03	13.87	13.70	13.54	13.37	13.21	13.05	12.88	12.72	12.55
13.93	13.77	13.61	13.45	13.29	13.13	12.98	12.82	12.66	12.50	12.34
13.68	13.53	13.37	13.22	13.06	12.91	12.76	12.61	12.45	12.30	12.15
13.43	13.28	13.13	12.99	12.84	12.69	12.54	12.39	12.25	12.10	11.95
13.20	13.05	12.91	12.77	12.62	12.48	12.34	12.19	12.05	11.91	11.76
12.97	12.83	12.69	12.56	12.42	12.28	12.14	12.00	11.86	11.72	11.58
12.76	12.63	12.49	12.36	12.22	12.09	11.96	11.82	11.68	11.55	11.42
12.55	12.42	12.29	12.16	12.03	11.90	11.77	11.64	11.51	11.38	11.25
12.35	12.23	12.10	11.98	11.85	11.73	11.60	11.47	11.35	11.22	11.10
12.16	12.04	11.92	11.80	11.67	11.56	11.44	11.31	11.19	11.07	10.95
11.97	11.86	11.74	11.62	11.50	11.39	11.27	11.15	11.03	10.92	10.80
11.80	11.69	11.57	11.46	11.34	11.23	11.12	11.00	10.89	10.78	10.66
11.63	11.53	11.41	11.30	11.18	11.08	10.97	10.86	10.75	10.64	10.52
11.47	11.36	11.25	11.14	11.03	10.93	10.83	10.72	10.61	10.50	10.39
11.31	11.21	11.10	11.00	10.89	10.79	10.69	10.59	10.48	10.37	10.26
11.16	11.06	10.95	10.86	10.75	10.65	10.56	10.46	10.35	10.24	10.14
11.01	10.91	10.81	10.72	10.62	10.52	10.43	10.33	10.22	10.12	10.02
10.87	10.78	10.68	10.59	10.49	10.39	10.30	10.20	10.10	10.00	9.90
10.74	10.65	10.55	10.46	10.36	10.27	10.18	10.08	9.98	9.88	9.79
10.61	10.52	10.42	10.33	10.24	10.15	10.06	9.97	9.87	9.77	9.68
10.48	10.39	10.30	10.21	10.12	10.03	9.94	9.85	9.76	9.66	9.57
10.36	10.27	10.18	10.10	10.01	9.92	9.83	9.74	9.65	9.56	9.47
10.25	10.16	10.08	9.99	9.90	9.82	9.73	9.64	9.56	9.47	9.38

The only one that differs appreciably from the others is the most modern one of all, that of JACOBSEN [2]). He, in his determination, placed a quantity of water in a large bottle and rotated it, by means of a motor, with its axis horizontal, until determination by means of the

[2]) J. P. JACOBSEN, Meddelelser fra Kommissionen for Havunder øgelser Serie: Hydrografi. Bind 1, No. 8. Kopenhagen, 1905.

Tab

No of cc. of Oxygen absorbed by 1000 cc. of sea-wate

t	Cl = 0	Cl = 1	Cl = 2	Cl = 3	Cl = 4	Cl = 5	Cl = 6	Cl = 7	Cl = 8	Cl = 9
−2	10.88	10.75	10.63	10.50	10.38	10.26	10.13	10.01	9.88	9.76
−1	10.58	10.46	10.34	10.22	10.10	9.98	9.86	9.74	9.62	9.50
0	10.29	10.17	10.06	9 94	9.83	9.71	9.59	9.48	9.36	9.25
1	10.02	9.90	9.79	9.68	9.57	9.45	9 34	9.23	9.12	9.01
2	9.75	9.64	9 53	9.43	9.32	9.21	9.10	8.99	8.88	8.78
3	9.50	9.39	9.29	9.19	9.08	8.98	8.87	8.77	8.66	8.56
4	9.26	9.16	9.06	8.95	8.85	8.75	8.65	8.55	8.45	8.35
5	9 03	8 93	8.83	8.73	8.64	8.54	8.44	8.34	8.24	8.14
6	8.81	8.71	8.62	8.52	8.43	8.33	8.24	8.14	8.05	7.95
7	8.60	8.50	8.41	8.32	8.23	8.14	8.04	7.95	7.86	7.77
8	8.40	8.31	8.22	8.13	8.04	7.95	7.86	7.77	7.68	7.59
9	8.21	8.12	8.03	7.95	7.86	7 77	7.69	7.60	7.52	7.43
10	8.02	7.94	7.85	7.77	7.69	7.60	7.52	7.44	7.36	7.27
11	7.84	7.76	7.68	7.60	7.52	7.44	7.36	7.28	7.20	7.12
12	7.68	7.60	7.52	7.44	7.36	7.29	7 21	7.13	7.05	6.97
13	7.52	7.44	7.36	7.29	7.21	7.14	7.06	6.98	6.91	6 83
14	7.37	7.29	7.21	7.14	7.07	7.00	6 92	6.85	6.77	6.70
15	7.22	7 15	7.07	7.00	6.93	6.86	6.79	6.72	6.64	6.57
16	7.08	7.01	6.94	6.87	6.80	6.73	6.66	6.59	6.52	6.45
17	6.94	6.88	6.81	6 74	6.67	6.60	6.54	6.47	6.40	6.33
18	6.81	6.75	6.68	6.62	6.55	6.48	6.42	6.35	6.28	6.22
19	6.69	6.63	6.56	6.50	6.44	6.37	6.30	6.24	6.17	6.11
20	6.57	6.51	6.44	6.38	6.33	6.26	6.19	6.13	6.07	6.00
21	6 46	6.40	6.33	6.27	6.22	6.15	6 09	6.03	5.96	5.90
22	6.35	6.29	6.23	6.17	6.11	6.04	5.98	5.92	5.86	5.80
23	6.24	6.18	6.12	6.06	6.01	5.94	5.88	5.82	5.77	5.71
24	6.14	6.08	6.02	5.97	5.91	5.84	5.79	5.73	5.67	5.61
25	6.04	5.99	5.92	5.87	5 81	5.75	5.69	5 64	5.58	5.52
26	5.94	5.89	5 82	5.77	5.71	5.66	5.60	5.55	5.49	5.43
27	5.84	5.79	5.73	5.67	5.62	5.57	5.51	5.46	5.40	5.34
28	5 75	5.69	5.64	5.58	5 53	5.48	5.42	5.37	5.31	5.25
29	5 66	5.60	5.55	5.49	5 44	5.39	5.33	5 28	5.22	5.16
30	5.57	5.51	5.46	5.40	5.35	5.30	5.24	5.19	5.13	5.07

well known WINKLER's titration method, showed a constant Oxygen value. As a matter of fact there is a theoretical objection to the adoption of this method which must not be overlooked. If this method be employed at all, it is necessary to ensure very efficient circulation between the air in the bottle and the outside air, because

1

rom a free dry Atmosphere of 760 mm. pressure

Cl = 10	Cl = 11	Cl = 12	Cl = 13	Cl = 14	Cl = 15	Cl = 16	Cl = 17	Cl = 18	Cl = 19	Cl = 20
9.63	9.51	9.39	9.26	9.14	9.01	8.89	8.76	8.64	8.52	8.39
9.38	9.26	9.14	9.02	8.90	8.78	8.66	8.54	8.42	8.30	8.18
9.13	9.01	8.90	8.78	8.66	8.55	8.43	8.32	8.20	8.08	7.97
8.89	8.78	8.67	8 56	8.44	8.33	8.22	8.11	8.00	7.88	7.77
8.67	8.56	8 45	8.34	8.23	8.12	8.02	7.91	7.80	7.69	7.58
8.45	8.35	8.24	8 14	8.03	7.93	7.82	7.72	7.61	7.51	7.40
8.24	8.14	8.04	7.94	7.84	7.74	7.64	7.53	7.43	7.33	7.23
8.05	7.95	7.85	7.75	7.65	7.56	7 46	7.36	7.26	7.16	7.07
7.86	7.76	7.67	7.57	7.48	7.39	7.29	7.20	7.10	7.01	6.91
7.68	7.59	7.50	7.40	7.31	7.22	7.13	7.04	6.95	6.85	6 76
7.51	7.42	7.33	7.24	7.15	7.06	6.97	6.89	6.80	6.71	6.62
7.34	7.26	7.17	7.09	7 00	6.91	6.83	6.74	6.66	6.57	6.48
7.19	7.10	7.02	6.94	6.85	6.77	6 69	6.60	6.52	6.44	6 35
7.04	6.96	6.88	6.80	6.71	6.63	6.55	6.47	6.39	6.31	6.23
6.89	6.82	6.74	6.66	6.58	6.50	6.43	6.35	6.27	6.19	6.11
6.76	6.68	6.61	6.53	6.46	6.38	6.31	6.23	6.15	6.08	6.00
6.63	6.55	6.48	6.41	6.34	6 26	6.19	6.11	6.04	5.97	5.89
6.50	6.43	6.36	6.29	6.22	6.14	6.07	6.00	5.93	5.86	5.79
6.38	6.31	6.24	6.17	6.10	6.03	5.96	5.89	5.82	5.76	5.69
6.26	6.20	6.13	6.06	5.99	5.93	5.86	5.79	5.72	5.66	5.59
6 15	6.09	6.02	5.96	5.89	5.83	5.76	5.69	5 63	5.56	5.49
6.05	5.98	5.92	5.86	5.79	5.73	5.66	5.60	5.53	5.47	5.40
5.95	5.88	5.82	5.76	5.69	5.63	5.56	5.50	5.44	5.38	5 31
5.85	5.78	5.72	5.66	5.59	5.53	5 47	5.41	5.35	5.29	5.22
5.75	5.68	5.62	5 56	5.50	5.44	5.38	5.32	5.26	5.20	5.13
5.65	5.59	5 53	5.47	5.41	5.35	5.29	5.23	5.17	5.11	5.04
5.55	5.50	5.44	5.38	5.32	5.26	5.20	5.14	5.09	5.03	4.95
5.46	5.41	5 35	5.29	5.23	5.17	5.12	5.06	5.00	4.95	4.86
5.37	5.32	5.26	5 20	5.14	5.09	5.03	4.97	4.92	4.86	4.78
5.28	5.23	5.17	5.11	5.06	5.00	4.94	4 89	4.83	4.78	4.70
5.19	5.14	5.08	5.02	4 97	4.91	4.86	4.80	4.75	4.69	4.62
5.10	5.05	4.99	4.93	4.88	4.83	4.77	4.71	4.66	4.60	4.54
5.01	4.96	4.90	4.85	4.79	4.74	4.68	4.63	4.58	4.52	4.46

the partial pressures of the Oxygen and Nitrogen within the bottle will otherwise alter. Oxygen is in fact twice as soluble as Nitrogen; and the result is that its original proportion in the air inside the bottle will be diminished and that of the Nitrogen will be increased by shaking with water, unless the air be continually renewed all the

Table 12

t	Nitrogen (Argon-free)		Oxygen	t	Nitrogen (Argon-free)		Oxygen
	Bohr & Bock (corrected)	Fox	Fox		Bohr & Bock (corrected)	Fox	Fox
−2	—	0.02439	0.05206	25	0.01471	0.01463	0.02890
−1	—	0.02383	0 05062	26	0.01444	0.01443	0.02842
				27	0.01420	0.01424	0 02794
0	0.02330	0.02328	0.04923	28	0.01396	0.01407	0.02751
1	0.02281	0.02275	0.04794	29	0.01373	0 01389	0.02708
2	0.02232	0.02224	0.04665				
3	0.02188	0.02175	0.04545	30	0.01348	0.01373	0.02665
4	0.02144	0.02128	0.04431	31	—	0.01358	0.02627
				32	—	0.01342	0.02590
5	0.02103	0.02083	0.04321	33	—	0.01328	0.02554
6	0.02062	0.02039	0.04215	34	—	0.01313	0.02519
7	0.02023	0.01997	0.04115				
8	0.01985	0.01956	0.04019	35	0.01241	0 01300	0.02485
9	0.01947	0.01916	0.03928	36	—	0.01286	0.02452
				37	—	0.01273	0 02420
10	0.01911	0.01878	0.03837	38	—	0.01261	0.02389
11	0.01878	0.01842	0.03751	39	—	0.01248	0.02359
12	0.01843	0.01808	0.03675				
13	0.01810	0.01774	0.03598	40	0.01154	0.01236	0.02330
14	0.01777	0.01742	0.03526	41	—	0.01224	0.02302
				42	—	0.01213	0.02275
15	0.01746	0.01710	0.03455	43	—	0.01201	0.02249
16	0.01716	0.01681	0.03388	44	—	0.01189	0.02224
17	0.01686	0.01653	0.03321				
18	0.01661	0.01625	0.03258	45	0.01084	0.01178	0.02100
19	0 01631	0.01599	0.03201	46	—	0.01166	0.02177
				47	—	0.01155	0.02155
20	0.01602	0.01574	0.03144	48	—	0.01143	0.02134
21	0.01575	0.01550	0.03091	49	—	0.01132	0.02114
22	0.01549	0.01527	0.03038				
23	0.01522	0.01505	0.02986				
24	0.01495	0.01483	0.02938	50	0.01035	0.01120	0.02095

time. As pointed out above, the gas-phase as well as the liquid-phase should always be analysed when employing these methods. It may be expected that this method would give too low values for Oxygen and too high values for Nitrogen. As a matter of fact this is just what the present writer found in using a method similar to that of JACOBSEN, in connection with some other work. If water be saturated with air in this way and then analysed, it is always found that the Nitrogen indicates a temperature lower than that of the saturation temperature and the Oxygen a higher temperature; but that if a current of air be drawn through the bottle (by means

of a water-pump) while the bottle is rotating, that this apparent temperature-difference found, tends to disappear.

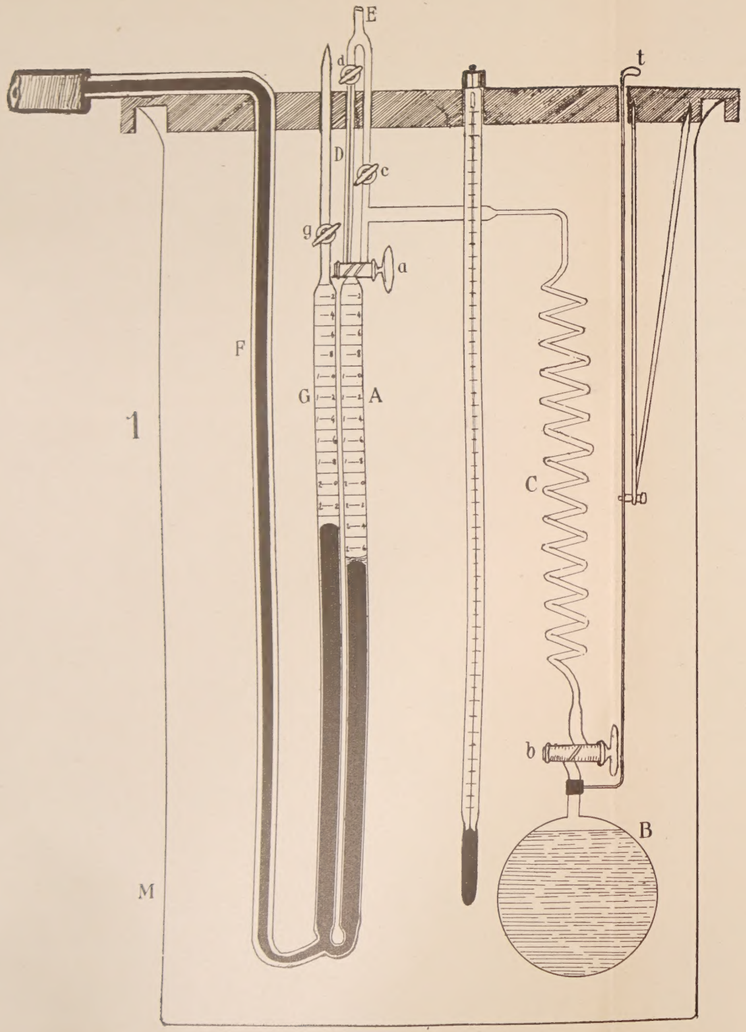
It appears that in JACOBSEN's determinations, there was no particular arrangement for the renewal of the air; to that extent the values may be expected to be low, and by a nearly constant percentage for different waters and temperatures, which might possibly be calculated, at all events approximately, from the dimensions of the bottle and the quantity of water taken.

The results of the observations here described, are collected in Tables 10 and 11 in the form in which they are perhaps most useful in Oceanography. Table 10 contains the number of cubic centimeters of Nitrogen (together with Argon) absorbed by the open sea per litre from the free atmosphere, as a function of the temperature and Chlorine concentration. Table 11 gives the number of cubic centimeters of Oxygen absorbed under the same conditions. In both cases it is assumed that the atmosphere always at all temperatures, has a pressure of 760 mm when freed from water vapour (and CO_2) and then always consists of 78.16 % Nitrogen, 0.94 % Argon and 20.90 % Oxygen by volume.

The absorption coefficients, in per cc. of distilled water, of Nitrogen and Oxygen of 760 mm. is of physical interest, in addition to the Oceanographical value of the Atmospheric partial pressures, which was the chief reason for the present investigation. They are therefore included here too, for the sake of completeness. As a matter of fact WINKLER's and BOHR and BOCK's determinations were made before the discovery of Argon; and if the former's figures refer also to Nitrogen prepared from air, as appears to be probable from what has already been said above, there have hitherto never been published any figures relating to pure Nitrogen.

Table 12 contains the absorption coefficients, per cc., of pure Nitrogen of 760 mm partial pressure, calculated from the observations of BOHR and BOCK and from those of the present writer; ESTREICHER's values for Argon have been adopted. In addition are included the values for Oxygen of 760 mm. partial pressure from the writer's measurements.

In conclusion the writer desires here to record his great indebtedness to Mr. L. VEGARD of the Physical Institute in the University of Christiania for invaluable help in the making of the measurements on which the present work is based.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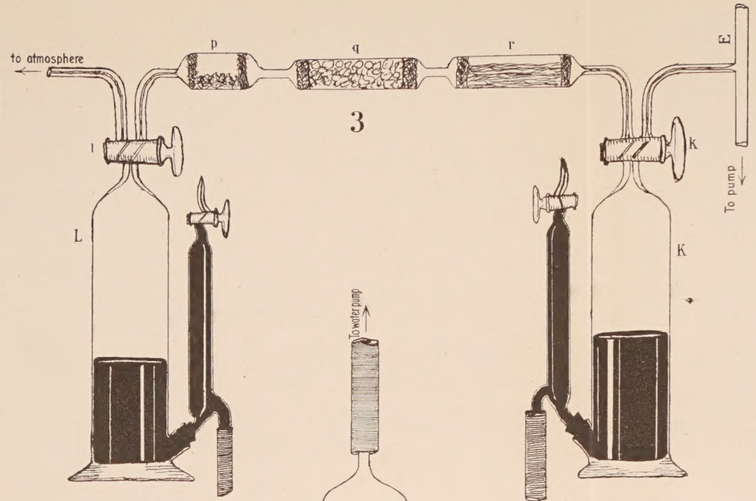
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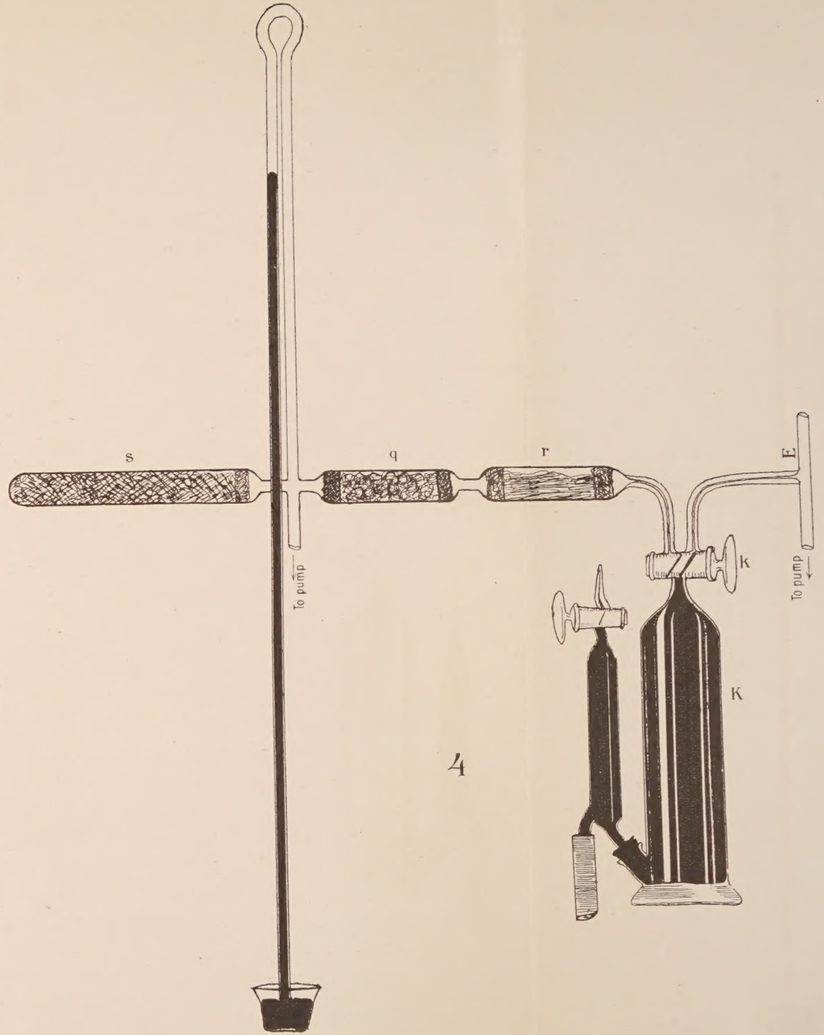
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Série A: Rapports et Procès-Verbaux des réunions
— B: Bulletin (trimestriel) des résultats acquis pendant les croisières périodiques etc.
— C: Publications de circonstance
— D: Bulletin statistique

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